Supporting information

Regulating Solution Spreading and Intermediate Phase Evolution for Large-Area Perovskite Films and Solar Modules

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Experimental section

Solution preparation: $FAPbI_3$ solutions were prepared by dissolving 0.7 M PbI_2 and 0.7 M FAI in DMF. Solvent additives with a volume percent of 5-30% were added into the solution to regulate the wettability. To make the solutions with single solid additive, MACl, PACl, PenACl, OACl, and PEACl was added into the $FAPbI_3$ solutions (solvent: DMF:IPA, volume ratio: 95:5), the molar ratio between $FAPbI_3$ and the additive is 1:0.6. To make the solutions with double solid additives, MACl+PACl, MACl+PenACl, MACl+OACl, and MACl+PEACl was added into the $FAPbI_3$ solutions. The molar ratio between perovskite and each additive is 1:0.3:0.3. The solutions with additives were stirred at room temperature for 30 min. The spiro-OMeTAD solution was made by dissolving 80 mg spiro-OMeTAD in 1 mL chlorobenzene, then add 30 μL 4-terbutylpyridine and 18 μL bis(trifluoromethane) sulfonimide lithium salt (520 mg/mL in acetonitrile).

Material characterization: The in-situ light absorption spectra were measured by using an Ocean Optics HR2000 spectrometer. The sample holder of the spectrometer is homemade to realize temperature control. The temperature of the substrate is ~45 °C during the drying process. The SEM images were taken with a Zeiss Merlin field emission SEM (FE-SEM) operated at an accelerating voltage of 5 kV. X-ray diffraction (XRD) patterns were obtained on D/MAX-TTRIII (CBO) with Cu Kα radiation (λ=1.54 Å). Photoluminescence spectra (PL) were measured on a LS55 photoluminescence spectrometer. Optical microscope images were measured using a LW200-3JT microscope.

Device fabrication: For the fabrication of small cells, cleaned ITO substrate (size: 1.5 cm*1.5 cm) was treated by UV-ozone for 15 min. SnO_2, perovskite, and spiro-OMeTAD layers were prepared in ambient air (RH: 30-40%, room temperature). SnO_2 dispersion (2.5% wt.%) was deposited onto the ITO substrate by spin coating at 4000 rpm for 30 s. The substrate with SnO_2 film is treated by UV-ozone for 10 min and transferred onto a 50 °C hot plate in air. 1.5 μL perovskite solution was dropped

into the center of the substrate. The solution can spread on the substrate spontaneously. The wet film was dried by N_2 blowing (flow speed: 5 L/min) for 10 s. Then the substrate was transferred onto a 150 °C hotplate and annealed for 15 min. Spiro-OMeTAD solution was spin-coated at 4000 rpm for 30 s in air. 80 nm Ag was deposited by thermal evaporation. The devices were transfer into a dry box and stored for 2 days before measurement. For the fabrication of solar modules, cleaned ITO substrate (size: 5 cm*5 cm) was treated by UV-ozone for 15 min. SnO_2 dispersion (2.5% wt.%) was deposited onto the ITO substrate by spin coating at 4000 rpm for 30 s. The substrate with SnO_2 film is treated by UV-ozone for 10 min and transferred onto a 40 °C hot plate in air. 25 μL perovskite solution (0.3 M) was dropped into the middle of the substrate by using a 5-channel pipette (5 μL solution for each channel). The solution can spread on the substrate spontaneously. The wet film was dried by N_2 blowing (using a N_2 tube with a diameter of 4 mm, the outlet is ~30 cm above the film, flow speed: 25 L/min) for 10 s. Then the substrate was transferred onto a 150 °C hotplate and annealed for 15 min. Spiro-OMeTAD solution was spin-coated at 4000 rpm for 30 s in air. A metal mask with grids (width: 70 μm) was put on the substrate, the gap between P1 line and the grid was adjusted to 80 μm. The P2 lines were made by using a normal doctor blade, which scratches along the metal grids, the pressure and moving speed of the blade is about 1 N and 2 cm/s, respectively. The substrate with mask was blown using N_2 to remove particles produced by scratching. Then 80 nm Ag was deposited by thermal evaporation. P3 lines were obtained by removing the mask.

Device measurements: A solar simulator (Enli Tech) was used as the light source. The light intensity (AM 1.5G, 100 mW/cm^2) was calibrated using a silicon reference cell (Enli SRC 2020, 2 cm × 2 cm) calibrated by NIM. The *J-V* and steady-state PCE were measured by using a digital source meter (Keithley 2400) in glovebox. The external quantum efficiency (EQE) spectra were measured by using a QE-R3011 measurement system (Enli Tech).

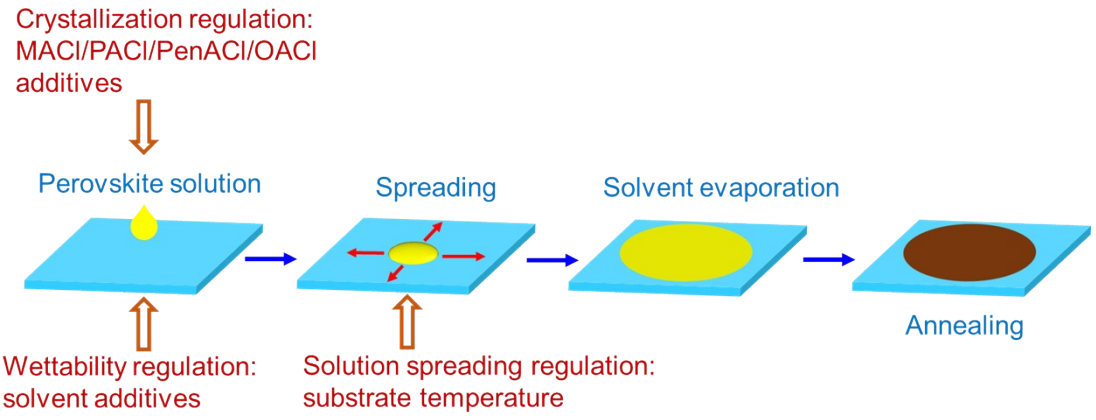


Figure S1. Preparation process and the strategies used to improve the spreading area and quality of the perovskite films in this work.

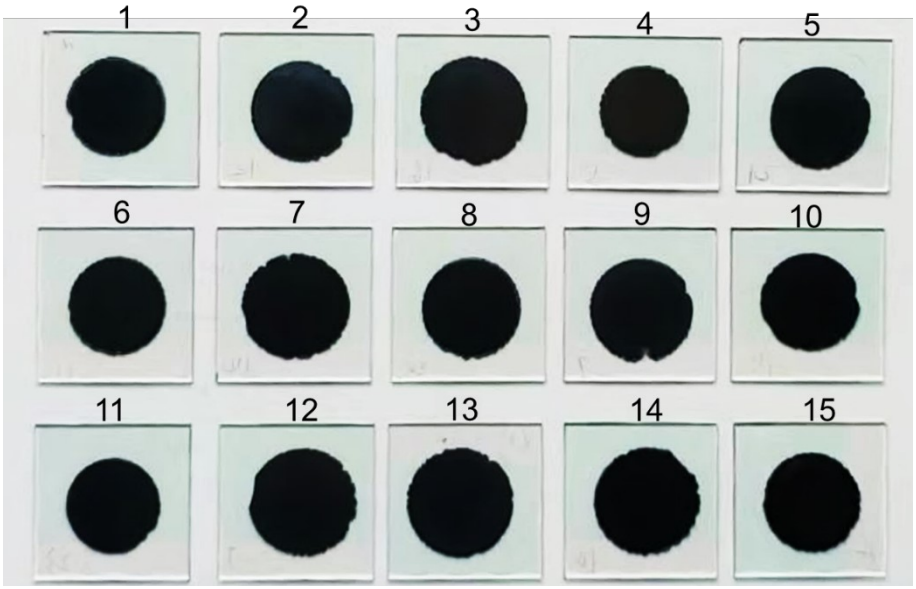


Figure S2. Photo of perovskite films made via self-spreading of solutions with different solvent additives.

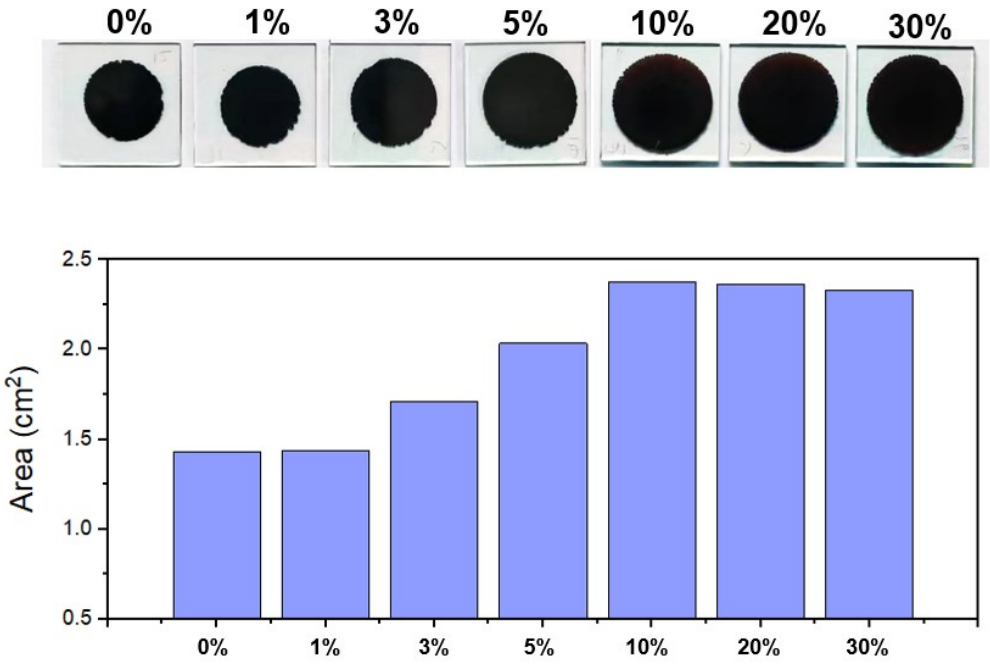


Figure S3. Effect of volume percent of IPA in DMF on area of the perovskite films made by self-spreading.

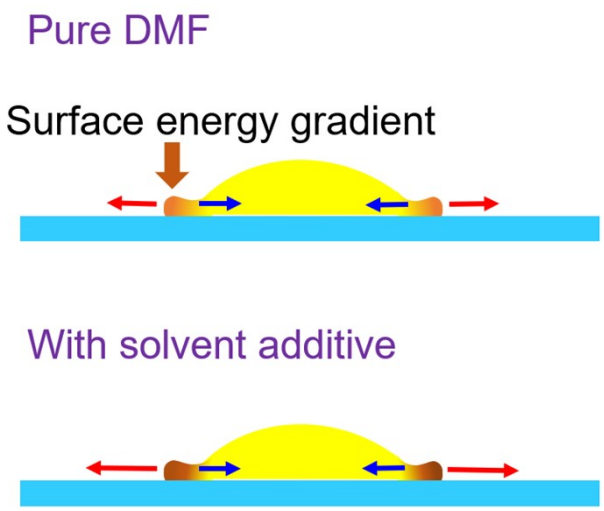


Figure S4. Illustration of the mechanism for improved spreading in solution with solvent additive. The solvent additive evaporates faster than DMF, increasing the concentration gradient and surface energy difference.

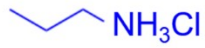
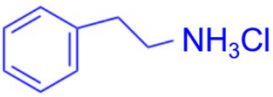
Chemical structure	Name (Abbreviation)
	Methylammonium chloride (MACl)
	Propylammonium chloride (PACl)
	Pentylammonium chloride (PenACl)
	Octylammonium chloride (OACl)
	Phenylethylammonium chloride (PEACl)

Figure S5. Chemical structure and name of the additives.

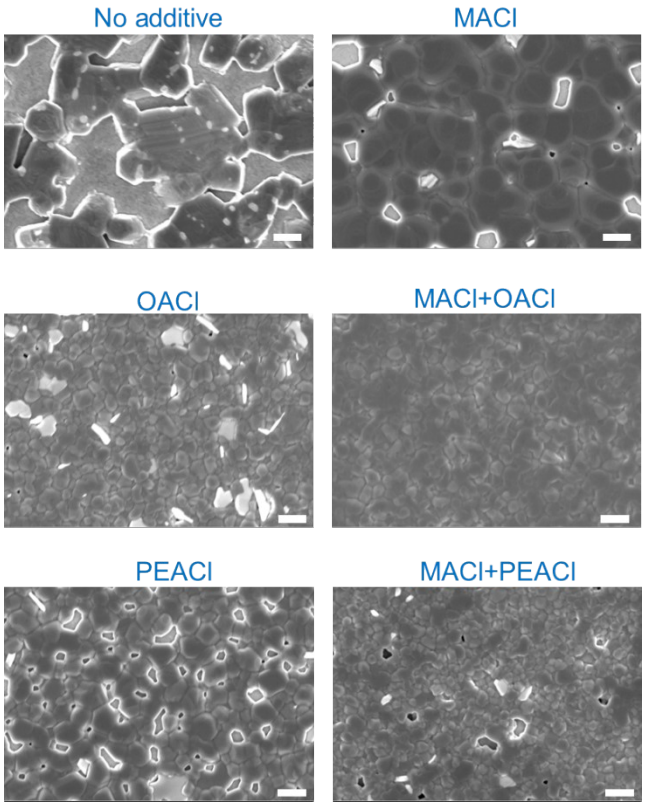


Figure S6. SEM images for perovskite films made by using different additives. Scale bar: 1 μm.

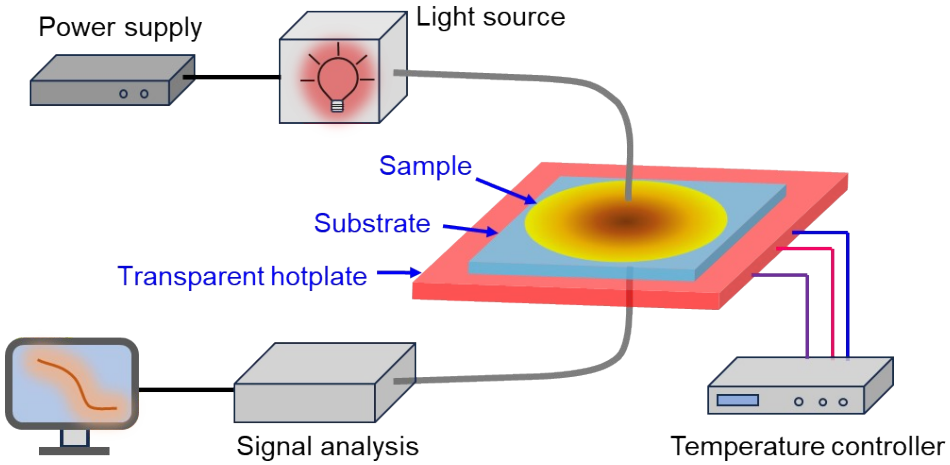


Figure S7. Illustration of the in-situ light absorption spectra measurement system.

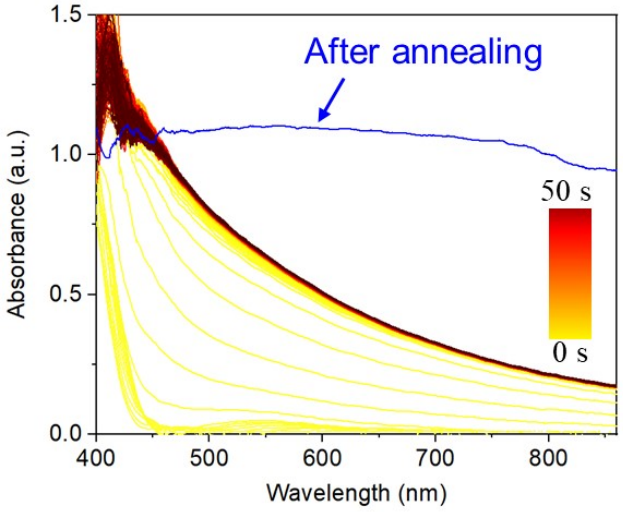


Figure S8. In-situ light absorption spectra for the crystallization process of $FAPbI_3$ solution without additives. The temperature of the substrate is 45 ℃.

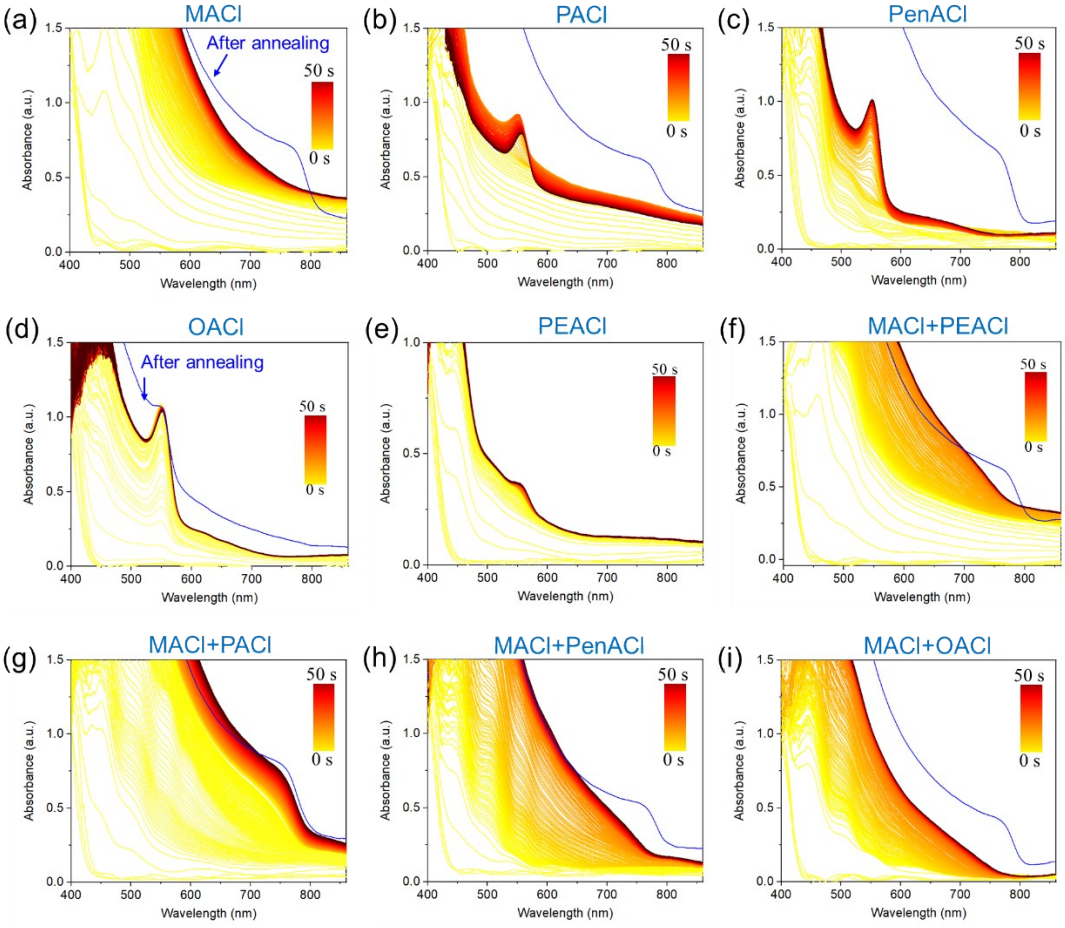


Figure S9. In-situ light absorption spectra for the drying process of perovskite solutions with different additives.

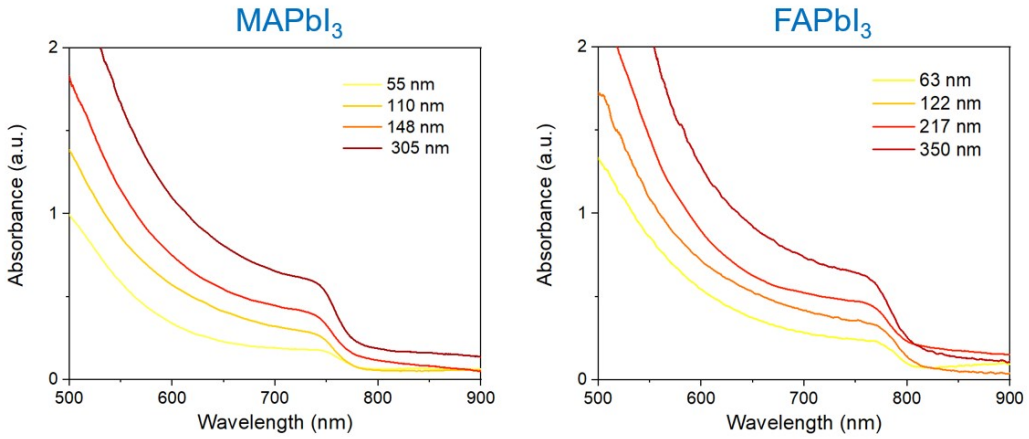


Figure S10. Light absorption spectra for $MAPbI_3$ and $FAPbI_3$ films with different thickness.

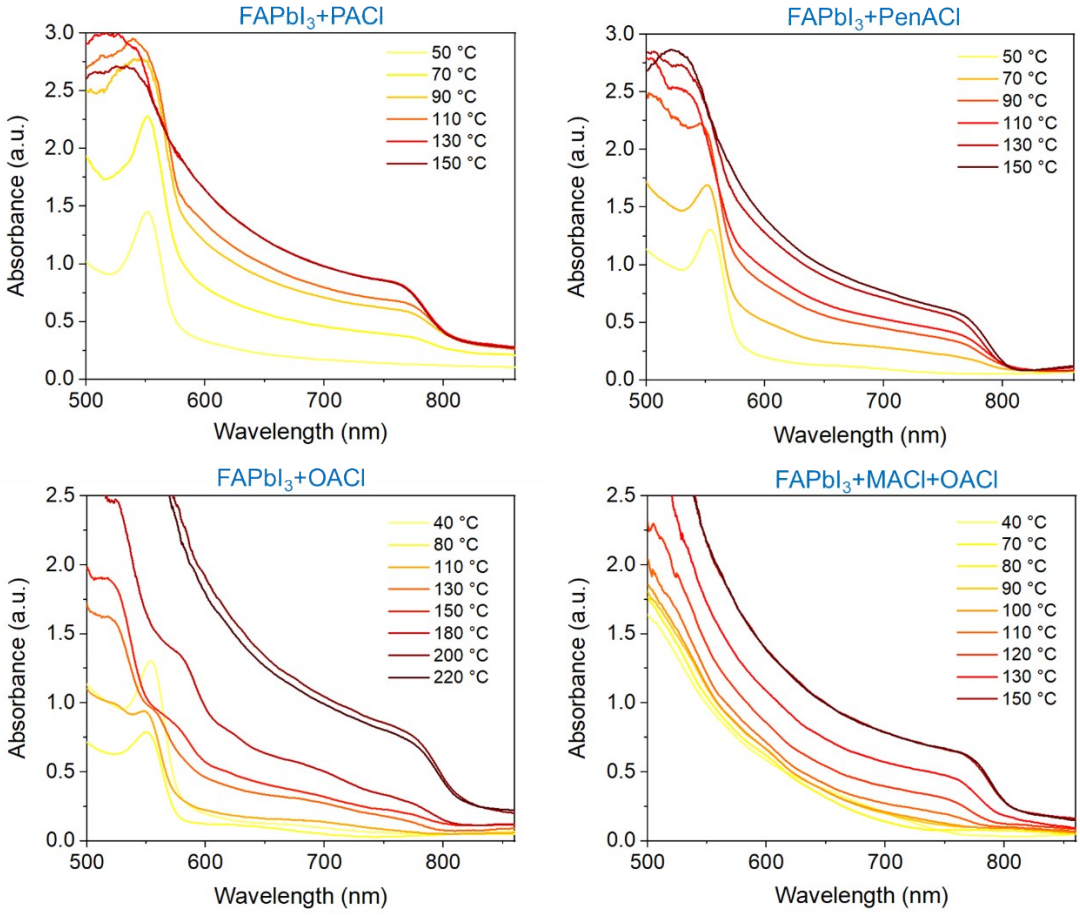


Figure S11. Light absorption spectra of films make by using solutions of $FAPbI_3$+PACl (molar ratio of 1:0.6), $FAPbI_3$+PenACl (molar ratio of 1:0.6), $FAPbI_3$+OACl (molar ratio of 1:0.6) and $FAPbI_3$+MACl+OACl (molar ratio of 1:0.3:0.3). The films were prepared by annealing the as-dried films at different temperature for 5 min.

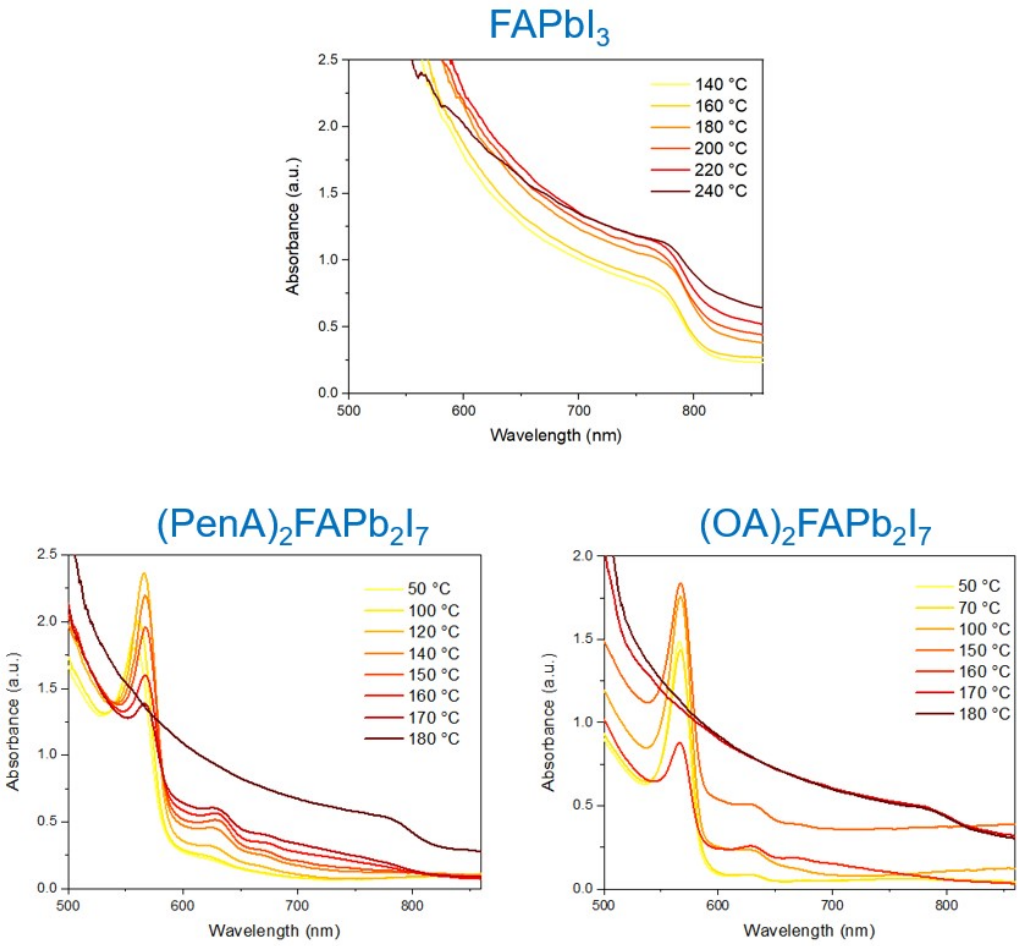


Figure S12. Light absorption spectra of perovskite films made by using solutions of $FAPbI_3$+MACl+OACl, $(PenA)_2FAPb_2I_7$, $(OA)_2FAPb_2I_7$. The films were prepared by annealing the as-dried film at different temperature for 5 min.

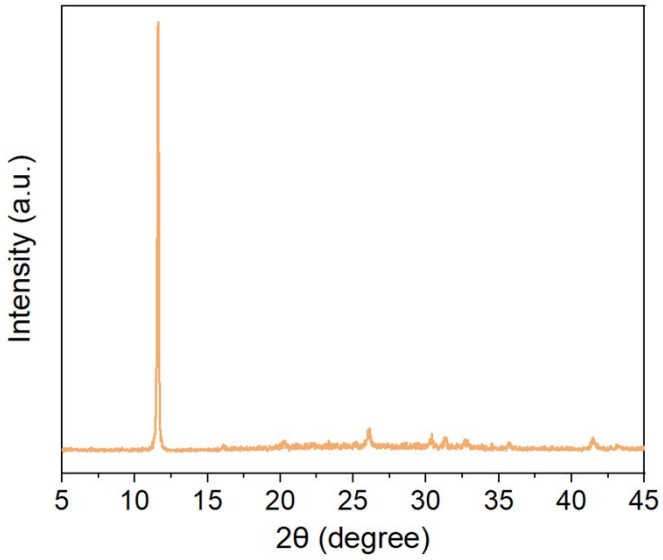


Figure S13. XRD pattern for as-dried film made by using $FAPbI_3$ solution without additive.

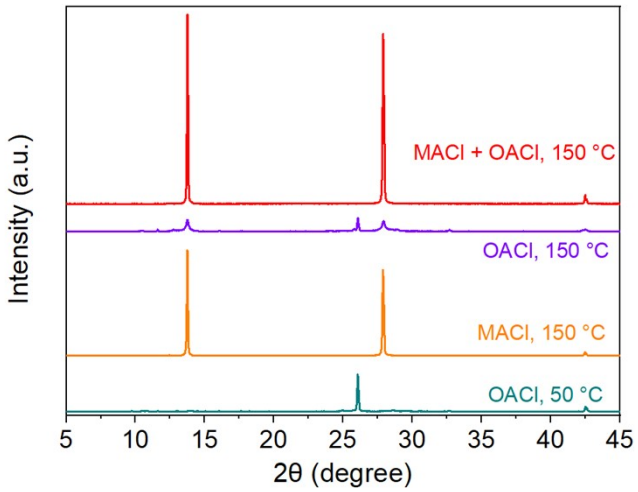


Figure S14. XRD patterns for the films made by using different additives in $FAPbI_3$ solutions after annealing at different temperature for 15 min.

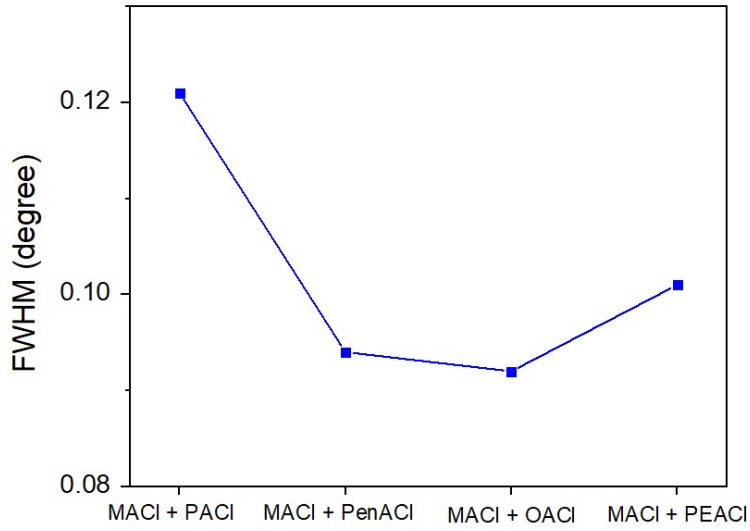


Figure S15. FWHM of the (100) peaks of perovskite films made by using different additives.

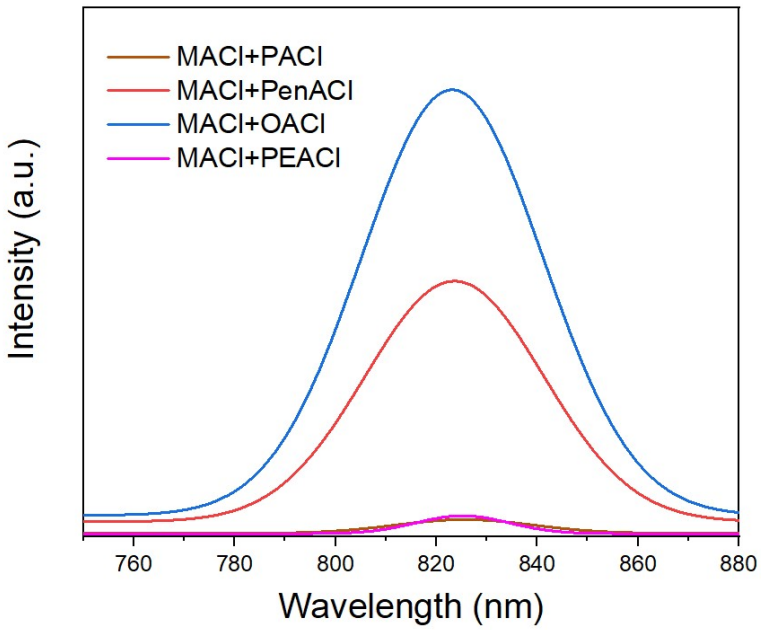


Figure S16. PL spectra for perovskite films made by using different additives.

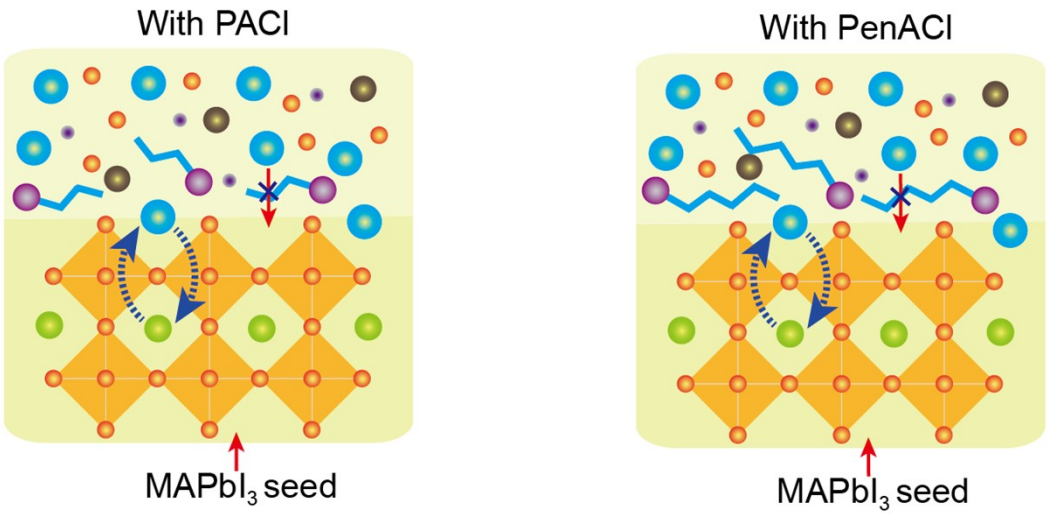


Figure S17. Illustration of the crystallization process for $FAPbI_3$ solution with PACl and PenACl.

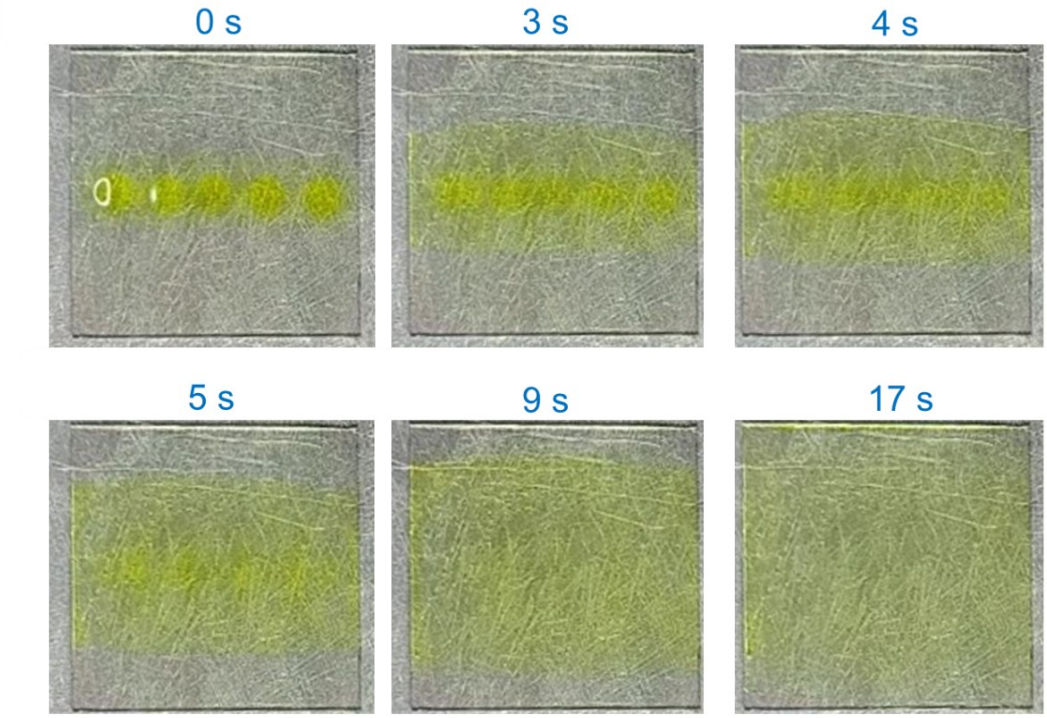


Figure S18. Spreading process of perovskite solution on a 5 cm * 5 cm substrate, which was put on a 40 °C hot plate.

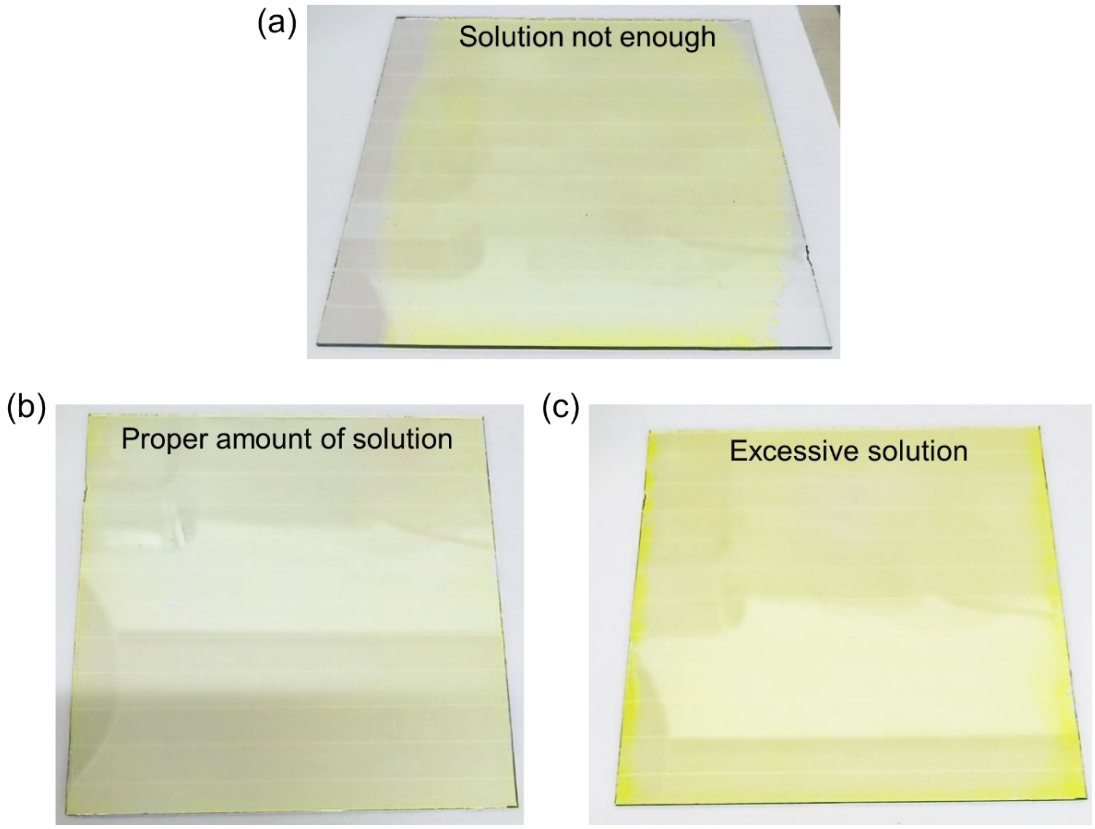


Figure S19. Photos for wet perovskite films prepared by using different amount of solution on 10 cm * 10 cm substrates.

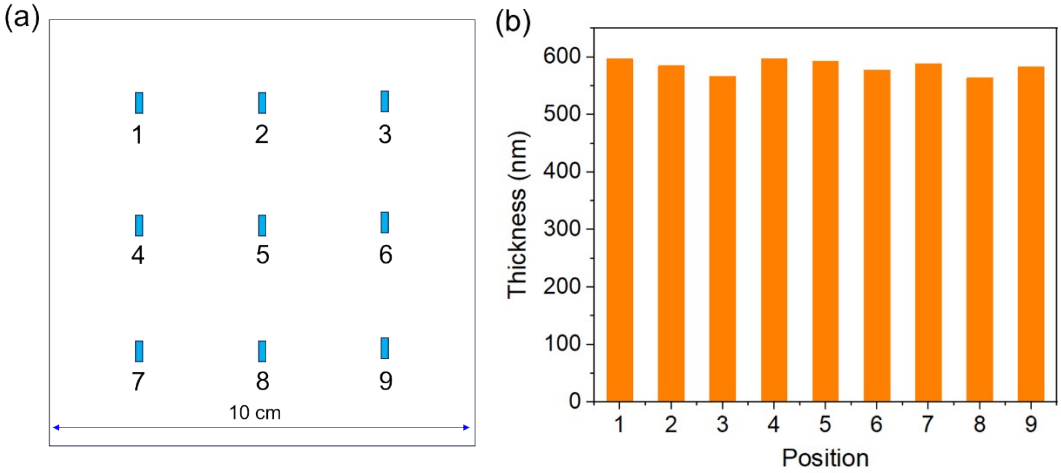


Figure S20. Positions for thickness measurement and the corresponding thickness value in a 10 cm×10 cm perovskite film.

Figure S21. Photo for a perovskite film prepared on a 7 cm * 10 cm flexible substrate by using the self-spreading method.

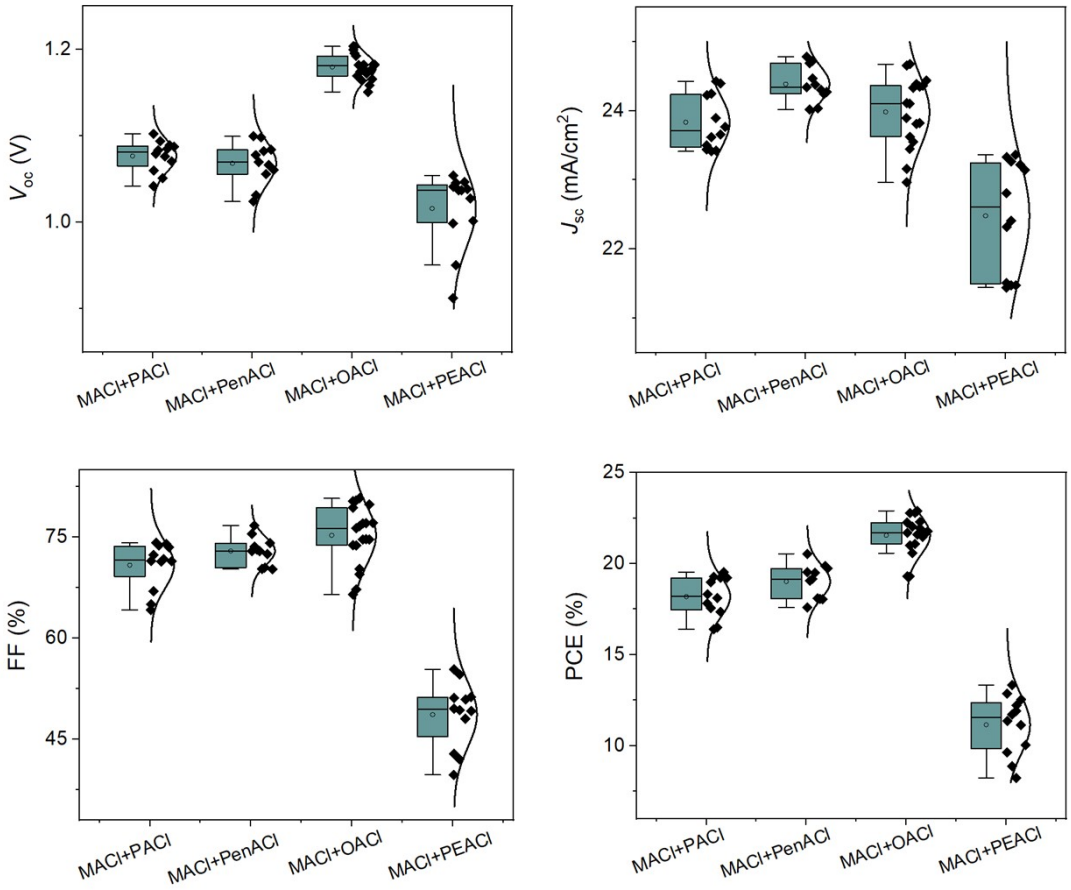


Figure S22. PCE of perovskite solar cells made by using different additives.

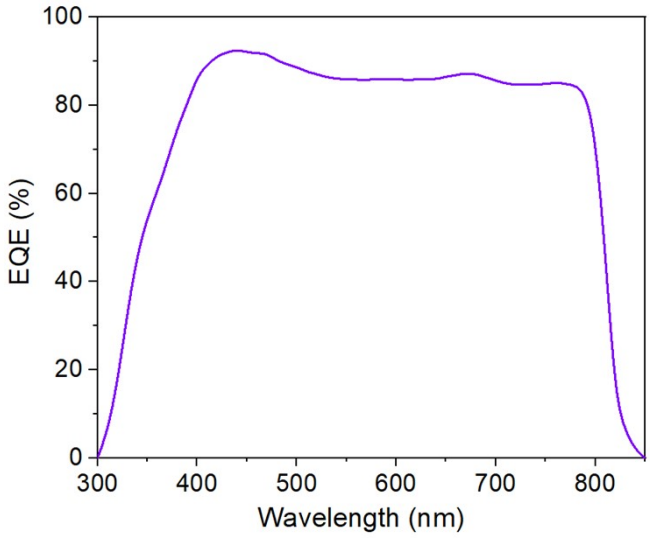


Figure S23. EQE spectrum for the champion solar cell.

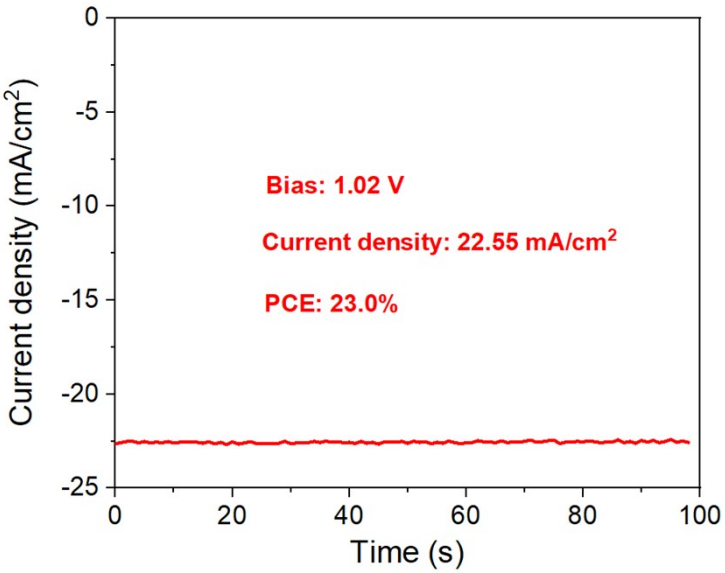


Figure S24. Steady-state PCE for the champion cell

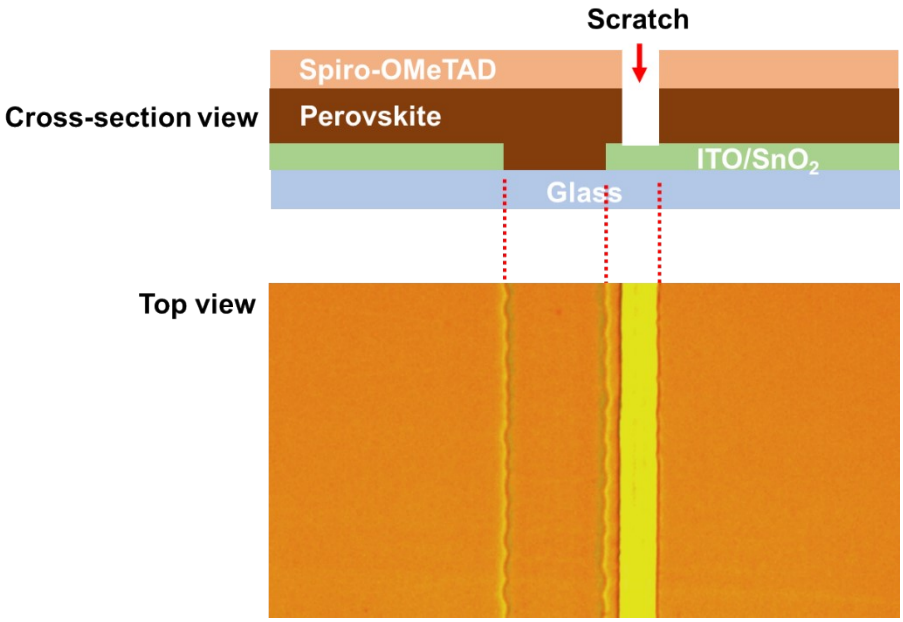


Figure S25. Optical microscopy image for the P2 line made by using mechanical scratch.

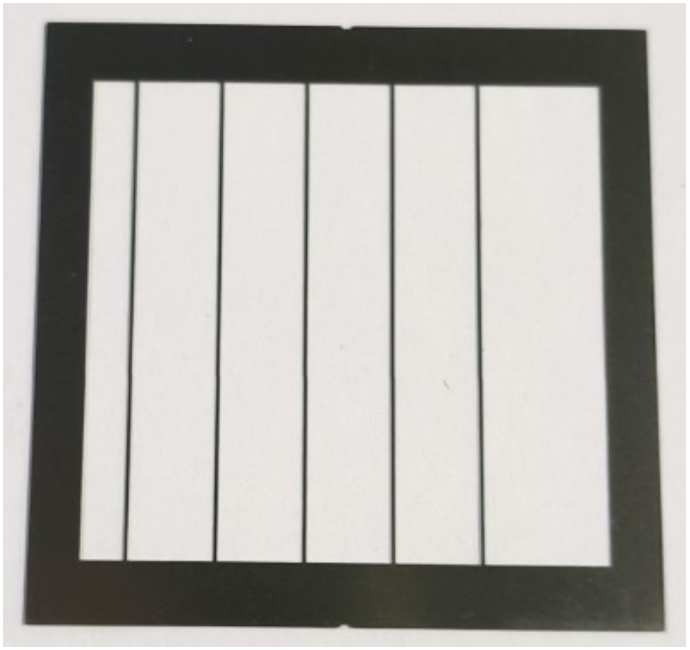


Figure S26. Photo of a mask (size: 5cm * 5 cm) for making perovskite modules.

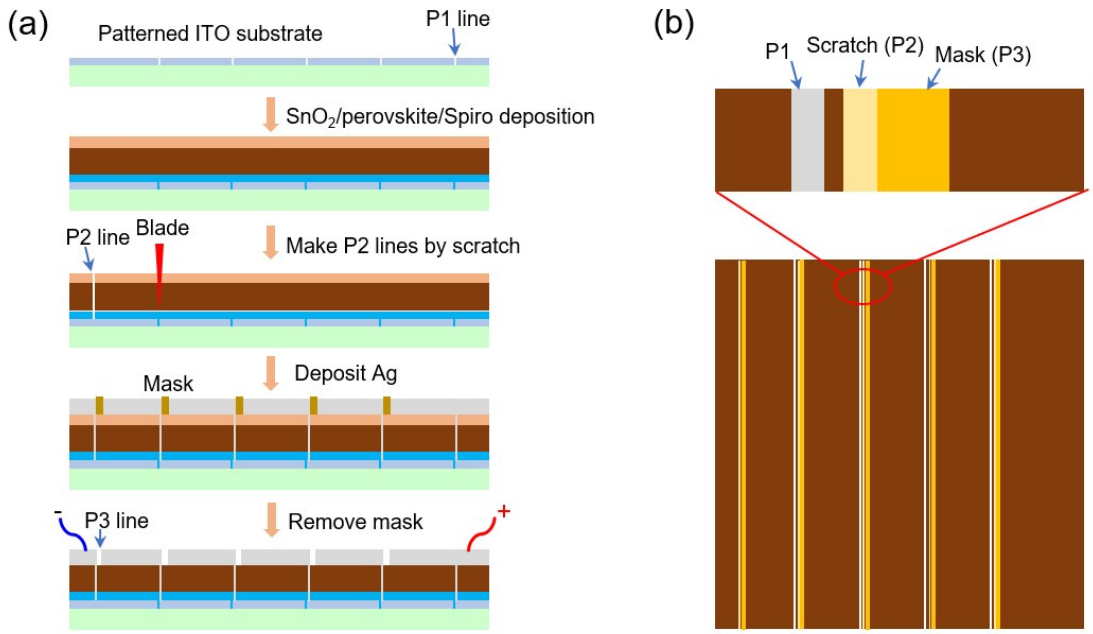


Figure S27. (a) Fabrication process of the perovskite solar modules. (b) Top view of perovskite film with mask grids before evaporation of Ag.

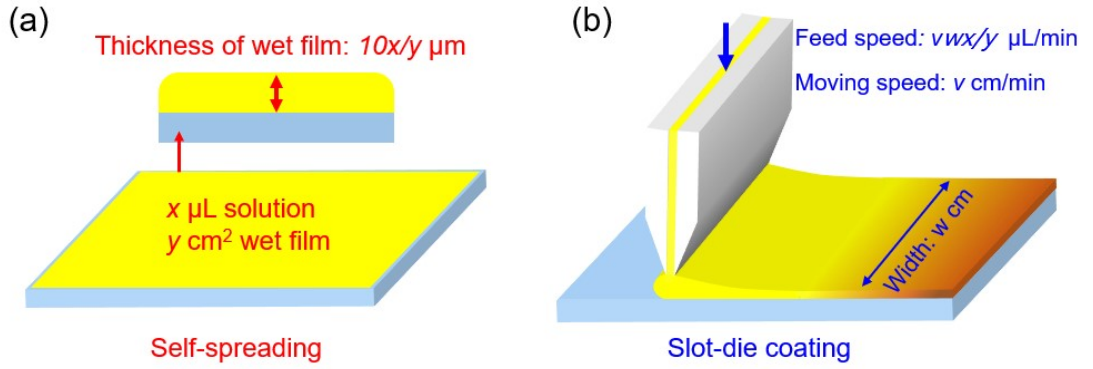


Figure S28. (a) Calculation of wet film thickness for a film made using self-spreading method. (b) Calculation of feed speed and moving speed in slot-die coating method to obtain the same film thickness with the self-spreading method.

Table S1. Properties of the solvents used in this work.

Solvent	Boiling Point (°C)	Surface Tension (mN/m @ 25°C)	Viscosity (cP @ 25°C)	Reichardt's ET(30) @ 25°C
DMF	153	37.1	0.92	43.8
Acetonitrile	82	29.3	0.34	46.0
iso-Propanol	82	21.7	2.04	48.6
2-Methoxyethanol	124	31.9	1.72	~52.0
Ethyl acetate	77	23.8	0.45	38.1
Chloroform	61	27.1	0.54	39.1
Diethyl ether	35	17.0	0.22	34.5
Chlorobenzene	132	33.6	0.80	37.5
Toluene	111	28.5	0.56	33.9
Acetone	56	23.5	0.32	42.2
Methanol	65	22.6	0.55	55.4
Ethanol	78	22.4	1.08	51.9
n-Propanol	97	23.8	1.95	50.7
n-Butanol	118	24.6	2.60	50.2
n-Pentanol	138	25.8	3.62	~49.5

Table S2. Performance of perovskite solar cells made by using different additives.

Additive	V_{oc} [V]	J_{sc} [mA/cm^2]	FF [%]	PCE [%]
Without	0.842	19.88	47.79	8.00
MACl	1.10	25.36	70.62	19.70
PACl	1.01	25.35	68.28	17.51
PenACl	0.985	24.04	68.89	16.31
OACl	1.02	24.69	65.54	16.55
PEACl	0.943	22.54	45.15	9.60

Table S3. Performance of perovskite solar cells made by using different combination of additives.

Additive	V_{oc} [V]	J_{sc} [mA/cm^2]	FF [%]	PCE [%]
MACl+PACl	1.09	24.42	73.56	19.53
MACl+PenACl	1.10	24.78	75.48	20.54
MACl+OACl	1.198	24.79	77.84	23.13
MACl+PEACl	1.05	23.32	54.60	13.33

Table S4**.** Summary of fabrication methods, GFF, and PCE (aperture area) for perovskite solar modules made using non-laser processing (P2 and/or P3 lines). The aperture area PCE is calculated from the active area PCE and the GFF, unless otherwise specified in the references.

Perovskite	P2	P3	GFF (%)	PCE (%)	Ref.
Spin coating	Mechanical scribing	Mechanical scribing	92.4	12.6	1
Spin coating	Laser scribing	Mechanical scribing	91	16.6	2
Blade coating	Laser scribing	Mechanical scribing	96	11	3
Thermal evaporation	Laser scribing	Mechanical scribing	90	12.3	4
Slot-die coating	Printing	Printing	75	11.0	5
Spin coating	Mechanical scribing	Mechanical scribing	87	17.9	6
Spin coating	Laser scribing	Mechanical scribing	94	10.9	7
Thermal evaporation	Mask	Mask	98	18.03	8
Spray coating	Mechanical scribing	Mechanical scribing	78.9	10.66	9
Self-spreading	**Mechanical scribing**	**Mask**	**97.3**	**19.88**	**This work**

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